

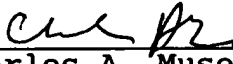
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cathode material separated by the separating device after adding either carbon or plastic to the cathode material and a decarbonizing device to heat the separated cathode material under an oxidized atmosphere and to oxidize and remove carbon contained in the valent metals either prior or following the reduction fusing process, thereby recovering the valent metals.

REMARKS

The amendment is made to insert reference to the parent applications and to conform the claims to the American practice.

Respectfully submitted,
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Process and System for Recovering Valent Metals from Refuse

Secondary Batteries

--PRIOR APPLICATIONS

This application is a division of U.S. Patent Application Serial No. 09/581,696 filed June 15, 2000 which is a 371 of PCT/JP99/05830 filed October 22, 1999.--

Field of Invention

The present invention is related to a process for recovering valent metals from refuse secondary batteries, and more specifically to a process and a system for recovering valent metals in a state of high purity from refuse secondary batteries, which are safe, simple, and economically-advantageous.

Background Art

In the past, for secondary batteries used for electric cars, lithium ion secondary battery, nickel-hydrogen secondary battery, nickel-cadmium secondary battery, lead storage cell and the like have been recommended. However, lithium ion secondary battery and nickel-hydrogen battery are considered as promising ones in view of high power density, long durability and high energy density particularly when required for electric cars.

When using these batteries, great amount of refuse secondary batteries, which contain great amount of valent metals, such as hydrogen-occluded alloy (cathode active substance), nickel and cadmium, are resulted, thus requiring recycling process to recover these valent metals from such refuse secondary batteries (dead batteries).

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rinse the crushed material obtained in the crushing process and the first sieving process to carry out the first sieving.

5. The recovering process for valent metals from refuse secondary batteries according to claim 4, characterized in that the process comprises a second sieving process to sieve the material remained over a sieve in the first sieving process, a second crushing process to crush the material remained over a sieve in the first sieving process and a third sieving process to sieve the crushed material obtained in the second crushing process.
6. The recovering process for valent metals from refuse secondary batteries according to claim 5, characterized in that the material sieved down in the second sieving process is mainly consisted of the separated cathode material.
7. The recovering process for valent metals from refuse secondary batteries according to claim 6, characterized in that the separated cathode material is mainly consisted of hydrogen-occluded alloy.
8. The recovering process for valent metals from refuse secondary batteries according to claim 5, characterized in that the process comprises a rubbing process to rub a mixture of a component remained over a sieve in the second sieving process and a component sieved down in the third sieving process, and a wet magnetic separation process to magnetically separate the crushed-material

under wet condition following to subjecting it to the rubbing process.

9. The recovering process for valent metals from refuse secondary batteries according to claim 8, characterized in that the component remained over a sieve in the third sieving process is mainly consisted of iron scrap, the magnetic component obtained in the wet magnetic separation process is mainly consisted of spumous nickel, and the non-magnetic component is mainly consisted of nickel hydroxide.

10. The recovering system for valent metals from refuse secondary batteries ^{of} ~~according to~~ ^{wherein} claim 2, ~~characterized~~ ^{device} ~~in that~~ the separating means comprises a cooling ^{means} to refrigerate the refuse secondary batteries with liquid nitrogen and a crushing ^{device} ~~means~~ to crush the refrigerated refuse secondary batteries to thereby recover the valent metals from the crushed material.

11. The recovering process for valent metals from refuse secondary batteries according to claim 1, characterized in that the process further contains a fusing process to fuse the separated cathode material separated in the separating process following to addition of calcium to the separated cathode material.

12. The recovering process for valent metals from refuse secondary batteries according to claim 11, characterized in that the additional amount of calcium is in a range of from 1 to 50 parts by weight based on

100 parts by wieght of the cathode material.

13. The recovering process for valent metals from refuse secondary batteries according to claim 11, characterized in that the addition of calcium is carried out following to the fusing of the separated cathode material.

14. The recovering process for valent metals from refuse secondary batteries according to claim 11, characterized in that nickel is added into the separated cathode material as a starting metal in the fusing process.

15. The recovering process for valent metals from refuse secondary batteries according to claim 11, characterized in that the fusing process is taken place under an atmosphere of an inactive gas.

16. The recovering process for valent metals from refuse secondary batteries according to claim 11, characterized in that the separated cathode material is crushed and separated after subjecting the refuse secondary batteries to refrigeration with liquid nitrogen during the mechanical separation process.

17. The recovering system for valent metals from refuse secondary batteries according ^{of} to claim 2, characterized ^{includes} ~~in that~~ the system comprises a fusing means to add calcium ^{to} ~~to~~ the separated cathode material separated by the separating means and ~~then~~ to fuse it to recover the valent metals.

18. The recovering process for valent metals from refuse secondary batteries according to claim 1, characterized in that the process comprises an oxidizing process to oxidize the separated cathode material separated in the separating process at a low temperature.

19. The recovering process for valent metals from refuse secondary batteries according to claim 18, characterized in that the oxidizing process is taken place at a temperature lower than 300°C and the oxygen concentration is adjusted to a range of from 5 to 25%.

20. The recovering process for valent metals from refuse secondary batteries according to claim 18, characterized in that nickel hydroxide as an anode material is added for the adjustment of the oxygen concentration.

21. The recovering process for valent metals from refuse secondary batteries according to claim 18, characterized in that the separated cathode material is one being crushed and separated by means of refrigerating the refuse secondary batteries with liquid nitrogen during the mechanical separation process.

22. The recovering system for valent metals from refuse secondary batteries ~~according to~~ claim 2, characterized ~~in that~~ ^{wherein} the system ~~comprises~~ ^{includes} an oxidizing means to oxidize the cathode material separated by the separating means at a ~~low~~ ^{lower than 300°C} temperature for recovering the valent metals.

23. The recovering process for valent metals from

refuse secondary batteries according to claim 1, characterized in that the process comprises a rare earth elements removing process to add an acid in an amount of 0.1-2.5 times equivalent based on the weight of the separated cathode material, which is required for dissolving the rare earth elements, in the separating process, a drying process to dry the cathode material from which the rare earth elements have been removed, and a fusing process to fuse the dried cathode material and then to recover the valent metals.

24. The recovering process for valent metals from refuse secondary batteries according to claim 23, characterized in that the oxidizing process to gradually oxidize the cathode material while bubbling air into the aqueous solution is constituted in a place prior to the drying process.

25. The recovering process for valent metals from refuse secondary batteries according to claim 23, characterized in that the fusing process is constituted with the addition of nickel as a starting metal into the material to be subjected to the fusing process.

26. The recovering process for valent metals from refuse secondary batteries according to claim 23, characterized in that the separated cathode material is one being crushed and separated by refrigerating the refuse secondary batteries with liquid nitrogen during the mechanical separation process.

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27. The recovering system for valent metals from refuse secondary batteries according to claim 2, characterized in that the system comprises a rare earth elements removing means to remove rare earth elements after adding an acid in an amount of 0.1-2.5 times equivalent based on the weight of the separated cathode material separated by the separating means, which is required for dissolving the rare earth elements, a drying means to dry the separated cathode material from which the rare earth elements have been removed, and a fusing means to fuse the dried cathode material to recover the valent metals.
28. The recovering process for valent metals from refuse secondary batteries according to claim 1, characterized in that the process comprises a reduction fusing process to reduce and fuse the separated cathode material separated in the separating process after adding either carbon or plastic into the cathode material and a decarbonizing process to heat the separated cathode material under an oxidized atmosphere to oxidize and remove carbon contained in the valent metals either prior or following to the reduction fusing process, thereby recovering the valent metals.
29. The recovering process for valent metals from refuse secondary batteries according to claim 28, characterized in that the separated cathode material comprises a refuse anode material and refuse sintered nickel.

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30. The recovering process for valent metals from refuse secondary batteries according to claim 28, characterized in that the process has a step of adding CaF_2 in the decarbonizing process.

31. The recovering process for valent metals from refuse secondary batteries according to claim 28, characterized in that the oxidizing agent is either of oxygen or nickel oxide.

32. The recovering process for valent metals from refuse secondary batteries according to claim 28, characterized in that the separated cathode material is prepared by crushing and separation of the refuse secondary batteries following to the refrigeration of the refuse secondary batteries with liquid nitrogen during the mechanical separation process.

33. The recovering system for valent metals from refuse secondary batteries according to claim 2, ^{whereby} characterized ^{includes} in that the system ^{comprises} a reduction fusing ^{device} means to reduce and fuse the separated cathode material separated by the separating ^{device} means after adding either carbon or plastic ^{to} into the cathode material and a decarbonizing ^{device} means to heat the separated cathode material under an oxidized atmosphere and to oxidize and remove carbon contained in the valent metals either prior or following ~~to~~ the reduction fusing process, thereby recovering the valent ~~metals~~.

34. The recovering process for valent metals from

refuse secondary batteries according to claim 1, characterized in that the refuse secondary battery is any of nickel-hydrogen secondary battery, refuse nickel-hydrogen secondary battery and nickel-cadmium secondary battery.

35. The recovering process for valent metals from refuse secondary batteries according to claim 1, characterized in that the valent metal is mainly consisted of hydrogen-occluded alloy, spumous nickel, nickel-hydroxide and iron scrap.

36. The recovering process for valent metals from refuse secondary batteries according to claim 1, characterized in that the recovering process to recover valent metals is taken place under an atmosphere of an inactive gas.

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